Device Model for Polymer Light Emitting Diodes: Effect of Temperature and Oxidation

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ABSTRACT

We present a temperature-dependent single carrier device model for polymer light-emitting diodes. The model includes both the injection of charge carriers over a barrier and the transport of charges across the device. To test the model, the temperature dependence of an LED based on the conjugated polymer poly[2-methoxy, 5-(2'ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) with indium tin oxide (ITO) and aluminum contacts was studied. Good agreement with experiment is found using a strongly field and temperature dependent mobility. Current-voltage characteristics were fitted over a temperature range from 100 K to 300 K using three parameters: the barrier to injection, the zero-field mobility, and the field dependence of the mobility. The resulting mobility parameters have an activation energy type form and are found to vary with temperature according to previously reported results. The barrier height to injection is found to decrease strongly between 300 K and 220 K, but decreases more slowly below 220 K. This reduction with temperature is found to relate to the red-shift of the absorption peak of MEH-PPV. The model is used to fit current-voltage characteristics of aged devices. The effect of photo-oxidation is well described by the model through a reduction of mobility at constant barrier height, giving insight into the effects of the creation of charge trapping carbonyl groups in the bulk polymer on injection and transport.

Keywords: poly(phenylene vinylene), light-emitting diodes, transport measurements, ITO, disorder, injection, oxidation

1. INTRODUCTION

Over the past decade polymer light emitting diodes (LEDs) have progressed rapidly from being a mere material science curiosity to forming the basis of a new generation of light, robust, efficient, self-luminescent and even flexible displays[1]. Whereas material and device parameters such as processibility, colour tunability and efficiency have advanced in great strides, much of the underlying physics of these quasi one-dimensional semiconductor systems is still debated. Numerous models describing the operation of these devices have been put forward, offering a qualitative and quantitative analysis of the device characteristics in terms of barrier to injection[2] and charge carrier mobility[3,4]. However, few attempts have been made to combine these two processes. Microscopic statistical models of the injection and transport processes possibly involved in LEDs have shown that to a first approximation bulk transport models do allow a qualitative analysis of the operation of these devices[5]. We demonstrate that Fowler-Nordheim tunnelling, which has previously been used to analyse current-voltage characteristics of the system studied here[2], cannot account for the strong temperature dependence observed for current-voltage characteristics and gives physically meaningless values for the barrier height. We then extend a macroscopic device model proposed by Davids et al.[6] to model current-voltage characteristics of LEDs over a wide range of temperatures.

Both the temperature dependence of current-voltage characteristics and photo-oxidation at constant temperature are strong tests of the device model and demonstrate that the three parameters used are sufficient to describe a wide range of phenomena observed in polymer LEDs. We find that even for significant barriers to injection such as from the indium tin oxide (ITO) anode to the highest occupied molecular orbital (HOMO) level, bulk transport effects do play a significant role in the device operation and a distinction between regimes of space charge limited (SCL) and injection limited (IL) operation is not always meaningful. A complete device model must hence take into account both injection and transport processes. We investigate this by comparing the role of the barrier to injection with that of the charge carrier mobility on the same sample. The model should adapt to a variation of the barrier to injection, which is lowered as the temperature is reduced and the band gap narrows, and also to a change in mobility at constant barrier height, which is observed when the sample is degraded in the presence of oxygen.

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2. EXPERIMENTAL

ITO substrates (Balzers, 20 Ω/) were masked, etched and then ultrasonicated in acetone and isopropanol. MEH-PPV was spin coated from chlorobenzene solution at concentrations of 4 mg/ml and spin speeds of 1000 rpm to give films of 150 nm thickness. Aluminum electrodes were evaporated onto the polymer layer at a pressure of 5×10^{-6} mbar. The devices were mounted on the cold finger of a closed loop helium cryostat and tested in vacuum at temperatures between 10 K and 300 K using a Keithley 2400 source measure unit. The temperature of the cold finger was measured with a silicon temperature sensor and controlled by an Oxford Instruments ITC4 temperature controller with a precision of 0.1 K. The temperature was varied in steps of 10 K and allowed to settle for at least 30 minutes between measurements. No effect of ohmic sample heating during operation was observed as the electroluminescence spectrum displayed no dependence on current density for the low currents (<0.4 A/cm^2) used in this experiment. Care was taken to ensure the device was not degraded during operation and current-voltage curves measured were found to be identical upon repeated cycling of the temperature. Film thicknesses were measured using a Tencor Alphastep with an accuracy of ± 5 nm. Absorption spectra of MEH-PPV were measured on a Perkin Elmer Lambda 19 spectrometer. The absorption peaks were determined by fitting five asymmetrical Gaussian line shapes with fixed width and asymmetry to the measured π absorption. For the study of the effect of mobility at constant barrier height the sample was degraded in the UV (355 nm) light of a Nd:YAG laser (10 Hz, 1 mJ, 10 ns pulses) for 1 minute.

3. SIMPLE INJECTION MODELS

It has previously been argued that LEDs in the configuration investigated here display purely IL current-voltage characteristics[2]. As the device efficiency can be correlated with the workfunction of the injecting electrode[2,7], it is clear that injection does play a significant role in device performance, which cannot be accounted for by SCL models alone. However, Fowler-Nordheim (FN) tunnelling theory alone is wholly inadequate to describe the strong increase in turn-on field with decreasing temperature observed in polymer LEDs, as tunnelling theory predicts a temperature independent current. Fig. 1 shows an example of two FN plots at 280 K and 20 K.

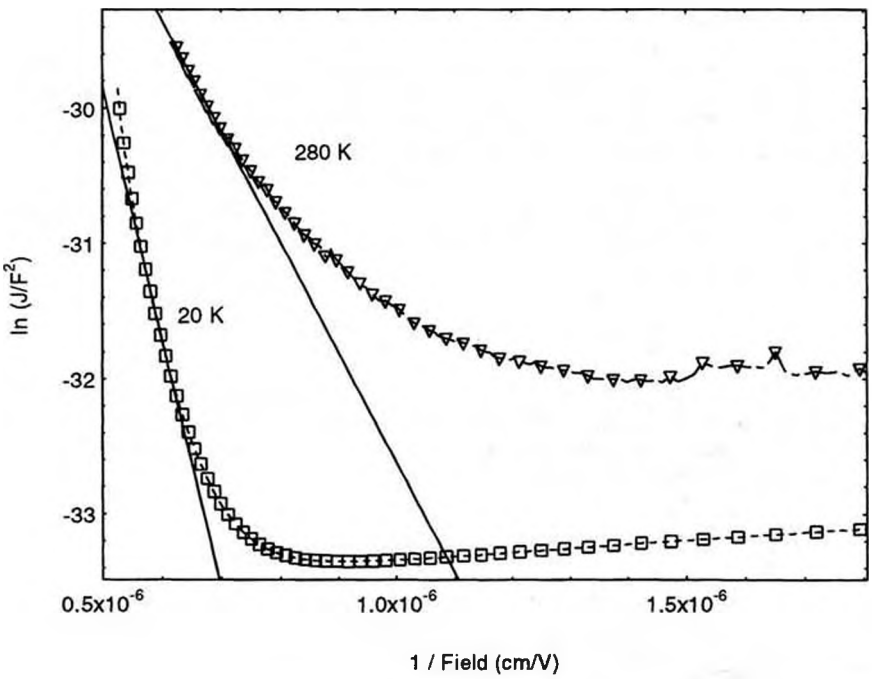

Fig. 1. *Fowler Nordheim plots of current-voltage characteristics of a single layer MEH-PPV LED with ITO and aluminum electrodes at 280 K and 20 K.*

Neither fits are good and it should be noted that the FN barrier height of approx. 0.2 eV found here at room temperature and reported previously[2] is much smaller than values obtained by direct measurements of the barrier by electroabsorption and

photo-emission techniques yielding values around 0.6 eV[8]. As the slope of the curves in Fig. 1 changes with temperature, it is interesting to plot the resulting FN barrier heights at different temperatures. The result is shown in Fig. 2 where it can be seen that the FN barrier height increases as the temperature decreases.

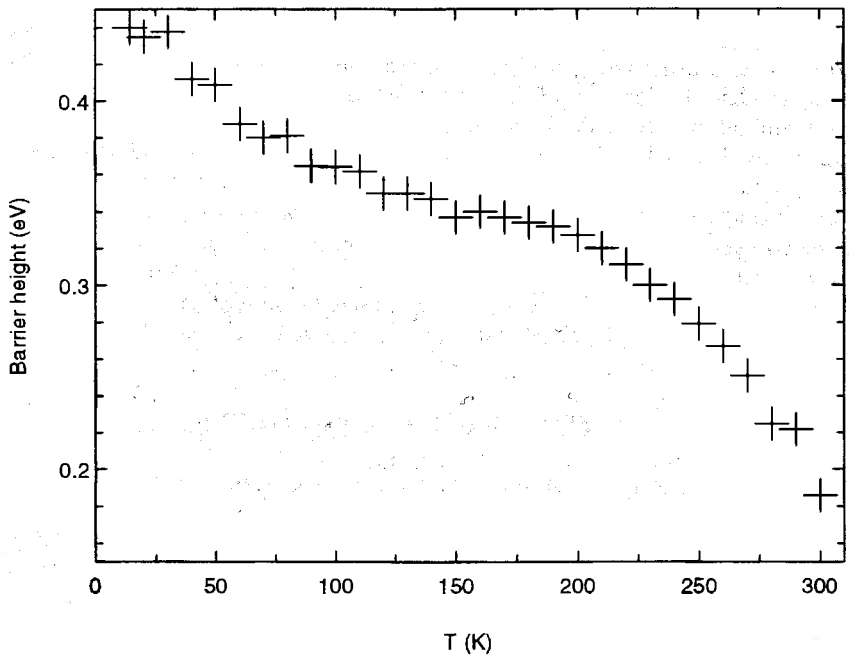

Fig. 2. *Plot of FN barrier height against temperature.*

It is interesting to note that the FN barrier height approaches the physical barrier height, the offset between the HOMO of the polymer and the workfunction of the metal, at low temperatures. At 10 K a tunnelling barrier height of 0.45 eV is determined. Room temperature photoemission experiments yield a barrier height of approx. 0.6 eV[8]. In contrast to the FN barrier, the physical barrier height is expected to decrease as the sample is cooled down as the band gap is found to shrink by up to 120 meV between room temperature and 10 K (see below). Hence at low temperatures a reduced barrier height of the order of 0.5 eV can be expected. The low temperature FN barrier height is thus significantly closer to the physical barrier height at low temperatures. A further problem with simple injection models is also the inability to predict the magnitude of the injected current density[2].

4. DEVICE MODEL

In the device model presented by Davids et al.[6] both injection and transport are included in one model. The boundary conditions are described by the linear superposition of currents arising from thermionic emission, time reversed thermionic emission and tunnelling. The strong degree of energetic disorder in the polymer and the hopping transport are accounted for by the inclusion of a field dependent mobility of the form (1)[4].

$$\mu_{(E)} = \mu_{(E=0)} \exp\left(\sqrt{\frac{E}{E_0}}\right) \quad (1)$$

We have demonstrated that the model by Davids et al. can be simplified significantly by considering only the drift current and modelling the device current in steady state by setting the time dependence of the current to zero[9]. The effect of the diffusion current is only expected to become of importance for low barrier heights, low temperatures and particularly low fields. As the main aim is to predict the behaviour of a useful working device, the high field limit required for significant current injection and electroluminescence is of greatest interest.

A suitable way to test the validity of the device model is to vary one device parameter and examine its effect on device operation and the parameters fitted to the measured characteristics. This was done successfully by Davids et al. for the case

of the barrier to injection[10]. They found that the model correctly fits the variation of barrier height when the workfunction of the majority carrier-injecting electrode is varied. Here we apply a further test of the model and attempt to fit to current-voltage characteristics obtained at different temperatures.

The continuity and drift equations were coupled to Poisson's equation and solved numerically by integrating across the device from the anode to the cathode. The boundary conditions are given by the injection term, which is approximated as a simple superposition of thermionic emission, time reversed thermionic emission and tunnelling current. These are clearly macroscopic injection processes derived for the case of sharp band edges and temperature independent band gaps. It was, however, recently shown that the device current calculated by statistical Monte Carlo simulations of carrier injection into a disordered polymer band is similar in functional field dependence to the macroscopic injection terms used[5] although the temperature dependence observed is not as strong as for the case of thermionic emission. The equations were solved across the whole parameter space for different temperatures and the best fits to the measured data were obtained by minimising the sum of the squares of the error.

5. RESULTS AND DISCUSSION

5.1. Mobility

The measured current-voltage characteristics were fitted using the three parameters in the device model. An example of data at 280 K and 100 K is shown together with fits on a linear and logarithmic scale in Fig. 3.

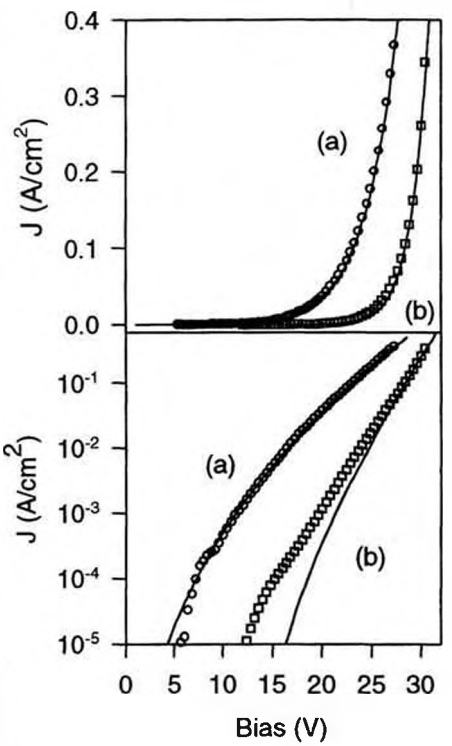

Fig. 3. *Fits to current-voltage characteristics for a 165 nm device: (a) at 280 K (φ=0.54 eV, $\mu_{(E=0)}$=3.9×10^{-6} cm^2/Vs, E_0=1.9×10^5 V/cm); (b) at 100 K (φ=0.41 eV, $\mu_{(E=0)}$=1.1×10^{-18} cm^2/Vs, E_0=1.9×10^3 V/cm).*

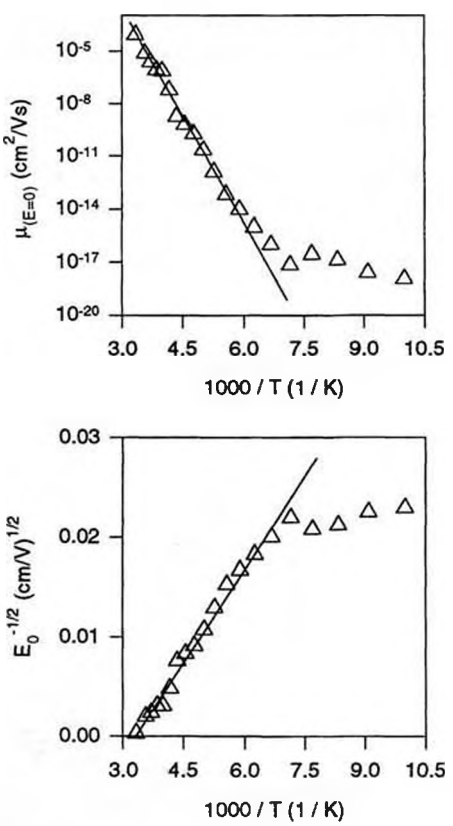

Fig. 4. *Temperature dependence of the mobility parameters.*

The fits are good over a large range of current at high temperatures, but deviate at low currents at low temperatures. This is thought to be predominantly related to the absence of diffusion currents in the model, which are of greater significance at low temperatures and for low barrier heights.

The temperature dependence of the mobility parameters fitted to the data is shown in Fig. 4. A temperature dependence of the form (2) for the zero-field mobility $\mu_{(E=0)}$ and (3) for the E_0 parameter has been demonstrated experimentally previously and discussed theoretically[4,11]:

$$\mu_{(E=0)} = \mu_0 \exp(-\frac{\Delta}{k_B T}) \quad (2)$$

$$\frac{1}{\sqrt{E_0}} = B(\frac{1}{k_B T} - \frac{1}{k_B T_0}) \quad (3)$$

where μ_0, Δ, T_0 and B are material constants related to the degree of disorder in the polymer.

The experimentally determined temperature dependence of the fitting parameters is in good agreement with equations (2) and (3). The $\mu_{(E=0)}$ parameter in Fig. 4 clearly follows an Arrhenius type decrease with decreasing temperature with an activation energy of Δ=0.78 eV. The B and T_0 parameters are found to be 5.5×10^{-4} eV $(cm/V)^{1/2}$ and 300 K, respectively. The activation energy is considerably larger than the value of 0.38 eV reported elsewhere for MEH-PPV devices spun from *p*-xylene[12]. However, Blom et al. have reported an activation energy for the hole mobility in a hole-only PPV device of 0.48 eV[4] and 0.59 eV[13]. This discrepancy shows that the activation energy determined can be sensitive to the details of the analysis involved. It has been shown that spin coated MEH-PPV films are highly amorphous and that the degree of order depends strongly on the solvent used[14]. A higher activation energy is hence expected for MEH-PPV devices spun from chlorobenzene in comparison to more ordered PPV films[11].

5.2. Barrier Height

The barrier heights for hole injection at the MEH-PPV/ITO interface obtained at room temperature agree well with values deduced from electroabsorption measurements of the built-in field in MEH-PPV/metal structures obtained by optical measurements[8]. The variation of the barrier height with temperature as deduced from the fit of the three parameters to the device model is plotted in Fig. 5 together with the position of the lowest energy vibronic feature of the absorption spectrum.

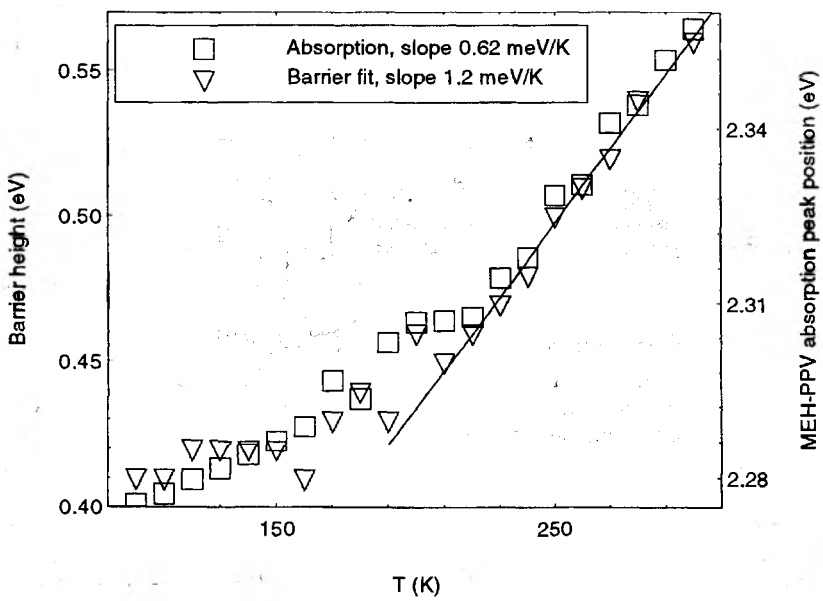

Fig. 5. *Decrease of barrier height with temperature compared to the red shift of the absorption of MEH-PPV.*

The barrier height decreases as the temperature is lowered, which is in accord with the observation of a reduction in bandgap at low temperatures. For temperatures below 150 K the fits become less sensitive to the barrier height for barriers below approx. 0.5 eV, indicating that space charge effects due to the extremely low mobilities form the current limiting mechanism. Remarkably, the shapes of the curves of both the absorption spectrum peak and the barrier height show a similar functional dependence on temperature. Both curves show two distinct regions above and below ~220 K. However, the shift of the absorption peak is only about half of the shift in barrier height. A direct comparison of absorption spectra at different temperatures shows a similar shift in the absorption tails which represent the tail states responsible for the transport of charge carriers, indicating that thermal broadening of the absorption spectra convoluted with the measured peak shift cannot account for this discrepancy. Also, assuming charge conjugation symmetry, one might expect the HOMO and LUMO levels to shift uniformly and the measured energetic shift of the absorption to correspond to twice the change in barrier height. The functional dependence on temperature of the three parameters is encouraging, as it demonstrates the consistency of the fitting procedure over a wide range of temperature. The fact that the change in barrier height with temperature is greater than implied by the absorption measurements may be a direct observation of the smaller temperature dependence of thermally assisted hopping injection into disordered systems in comparison to thermionic emission theory[5].

6. EFFECT OF AGEING

A further test of the model alongside the temperature dependence is to establish the capability to describe intrinsic variations of the device parameters, such as the majority charge carrier mobility. The fact that conjugated polymers are extremely sensitive to oxidation, which leads to conjugation breaking and the formation of charge trapping carbonyl groups, is well documented in the literature[15]. A comprehensive device model is required to describe device operation not only for pristine devices but also, and from the point of practical applications more importantly, of stored, aged and operated devices in order to understand the reasons behind degradation of polymer LEDs. We investigate here the case of artificially aged LEDs, which were exposed to the UV radiation of a laser. We find that this induced ageing has a similar result on device characteristics as prolonged storage in air, which is of significant interest regarding shelf life of devices[9]. Fig. 6 shows the current-voltage characteristic of an LED at room temperature before and after degradation.

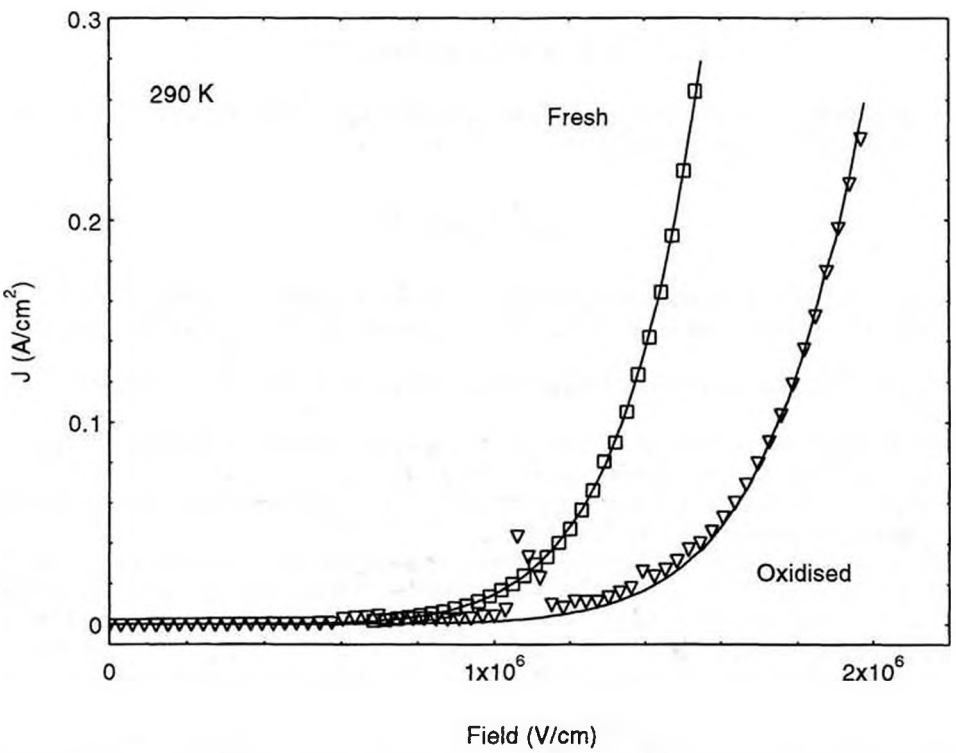

Fig. 6. *Effect of photo-oxidation on LED current-voltage characteristics (symbols) and corresponding model fits (solid lines) at room temperature.*

It is seen that the turn-on voltage increases by over 30 % after oxidation, which is fitted accurately by the model. The fitting parameters for the fresh sample are {φ=0.55 eV, $\mu_{(E=0)}$=6.9×10^{-6} cm^2/Vs, E_0=2.3×10^5 V/cm} and for the oxidised sample {φ=0.55 eV, $\mu_{(E=0)}$=2.5×10^{-7} cm^2/Vs, E_0=1.0×10^5 V/cm}. The model hence suggests that the change in current-voltage characteristics is due to a change in mobility with no significant variation of the barrier height. As discussed above, the large barrier to injection has traditionally been used to argue for a description of the device characteristics in terms of injection limited models. Our results however clearly demonstrate that even in the limit of large barriers to injection the low mobility of conjugated polymers is still a significant factor determining device operation and is vital in understanding practical effects such as device ageing.

7. CONCLUSIONS

We have demonstrated the importance of the inclusion of both space charge and injection effects in a complete single carrier device model for polymer LEDs. The fitting parameters are found to have distinct functional dependences on temperature. The zero-field mobility $\mu_{(E=0)}$ follows an Arrhenius type activation. Likewise the E_0 parameter has a functional dependence on temperature similar to previously reported results in another PPV derivative[4]. It is interesting to note that the barrier height to injection determined by the model has a functional dependence on temperature similar to the shift of the absorption of the polymer, although the decrease with temperature is overestimated by the model. These results suggest that it is indeed possible to fit these parameters meaningfully to current-voltage measurements. The significance of the barrier height for hole injection from ITO into the HOMO level of MEH-PPV in the model highlights the recent discovery that the barrier to hole injection is the efficiency limiting factor in devices with calcium cathodes[7]. The model hence provides a simple means for estimating the barrier height and optimising device structures to obtain more balanced injection. We have also demonstrated that the model successfully describes one of the most important device degradation mechanisms in the form of photo-oxidation. We find that an aged device is well described by a reduction in mobility with constant barrier to injection. This not only demonstrates the important interplay between mobility and barrier height in most device configurations, but also provides a useful tool for in-situ analysis of the quality and stability of the device.

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